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<p>(21) International Application Number: PCT/US99/30071 (22) International Filing Date: 15 December 1999 (15.12.99) (30) Priority Data: 09/212,774 16 December 1998 (16.12.98) US (71) Applicant: BATTELLE MEMORIAL INSTITUTE [US/US]; Pacific Northwest Division, Intellectual Property Services, P.O. Box 999, Richland, WA 99352 (US). (72) Inventor: AFFINITO, John, D.; 2718 Kyle Road, Kennewick, WA 99338 (US). (74) Agent: MAY, Stephen, R.; Battelle Memorial Institute, Pacific Northwest Division, Intellectual Property Services, P.O. Box 999, MSIN: K1-53, Richland, WA 99352 (US).</p>		<p>(81) Designated States: JP, KR, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: PLASMA ENHANCED POLYMER DEPOSITION ONTO FIXTURES</p> <div data-bbox="292 1155 1234 1680"> </div> <p>(57) Abstract</p> <p>Generally, the method of the present invention has the steps of (a) flash evaporating a liquid monomer forming an evaporate; (b) passing the evaporate to a glow discharge electrode creating a glow discharge monomer plasma from the evaporate; and (c) cryocondensing the glow discharge monomer plasma on a fixture and crosslinking the glow discharge plasma thereon, wherein the crosslinking results from radicals created in the glow discharge plasma and achieves self curing.</p>		

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PLASMA ENHANCED POLYMER DEPOSITION ONTO FIXTURES

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FIELD OF THE INVENTION

The present invention relates generally to a method of making plasma polymerized films on a fixture.

10 As used herein, a fixture is a discrete item. Examples include but are not limited to plumbing fixtures, cabinetry fixtures, tools, optical fixtures including reflectors, light covers, solar collectors and combinations thereof which are clearly distinct from a continuous item for example a sheet, wire, or rope.

As used herein, the term "(meth)acrylic" is defined as "acrylic or
15 methacrylic". Also, "(meth)acrylate" is defined as "acrylate or methacrylate".

As used herein, the term "cryocondense" and forms thereof refers to the physical phenomenon of a phase change from a gas phase to a liquid phase upon the gas contacting a surface having a temperature lower than a dew point of the gas.

20

BACKGROUND OF THE INVENTION

The basic process of flash evaporation is described in U.S. patent 4,954,371 herein incorporated by reference. This basic process may also be
25 referred to as polymer multi-layer (PML) flash evaporation. Briefly, a radiation polymerizable and/or cross linkable material is supplied at a temperature below a decomposition temperature and polymerization temperature of the material. The material is atomized to droplets having a droplet size ranging from about 1 to about 50 microns. An ultrasonic atomizer is generally used. The droplets are
30 then flash vaporized, under vacuum, by contact with a heated surface above the boiling point of the material, but below the temperature which would cause pyrolysis. The vapor is cryocondensed on a substrate then radiation polymerized or cross linked as a very thin polymer layer. The material may

include a base monomer or mixture thereof, cross-linking agents and/or initiating agents. A disadvantage of the flash evaporation method with radiation cross linking is that it requires two sequential steps, cryocondensation followed by curing or cross linking, that are both spatially and temporally separate. A
5 disadvantage of this radiation crosslinking method is the time between cryocondensation and curing permitting the cryocondensed monomer to flow or run, especially on fixtures having irregular non-flat geometry, leading to non-uniformity of coating (**FIG. 1a**) so that the coating surface **150** is geometrically different from the substrate surface **160**. Reducing surface temperature can
10 reduce the flow somewhat, but should the monomer freeze, then cross linking is adversely affected. Using higher viscosity monomers is unattractive because of the increased difficulty of degassing, stirring, and dispensing of the monomer

The basic process of plasma enhanced chemical vapor deposition (PECVD) is described in THIN FILM PROCESSES, J.L. Vossen, W. Kern,
15 editors, Academic Press, 1978, Part IV, Chapter IV - 1 Plasma Deposition of Inorganic Compounds, Chapter IV - 2 Glow Discharge Polymerization, herein incorporated by reference. Briefly, a glow discharge plasma is generated on an electrode that may be smooth or have pointed projections. Traditionally, a gas inlet introduces high vapor pressure monomeric gases into the plasma region
20 wherein radicals are formed so that upon subsequent collisions with the substrate, some of the radicals in the monomers chemically bond or cross link (cure) on the substrate. The high vapor pressure monomeric gases include gases of CH₄, SiH₄, C₂H₆, C₂H₂, or gases generated from high vapor pressure liquid, for example styrene (10 torr at 87.4 °F (30.8 °C)), hexane (100 torr at 60.4
25 °F (15.8 °C)), tetramethyldisiloxane (10 torr at 82.9 °F (28.3 °C) 1,3,-dichlorotetra-methyldisiloxane) and combinations thereof that may be evaporated with mild controlled heating. Because these high vapor pressure monomeric gases do not readily cryocondense at ambient or elevated temperatures, deposition rates are low (a few tenths of micrometer/min maximum) relying on
30 radicals chemically bonding to the surface of interest instead of cryocondensation. The low deposition rate is not useable in a high rate industrial application. Remission due to etching of the surface of interest by the plasma

competes with deposition of the radicals. Lower vapor pressure species have not been used in PECVD because heating the higher molecular weight monomers to a temperature sufficient to vaporize them generally causes a reaction prior to vaporization, or metering of the gas becomes difficult to control, either of which is inoperative.

According to the state of the art of making plasma polymerized films, PECVD and flash evaporation or glow discharge plasma deposition and flash evaporation have not been used in combination. However, plasma treatment of a substrate using glow discharge plasma generator with inorganic compounds has been used in combination with flash evaporation under a low pressure (vacuum) atmosphere as reported in J.D. Affinito, M.E. Gross, C.A. Coronado, and P.M. Martin, A Vacuum Deposition Of Polymer Electrolytes On Flexible Substrates. "Paper for Plenary talk in A Proceedings of the Ninth International Conference on Vacuum Web Coating", November 1995 ed R. Bakish, Bakish Press 1995, pg 20-36., and as shown in FIG. 1b. In that system, the plasma generator 100 is used to etch the surface 102 of a moving substrate 104 in preparation to receive the monomeric gaseous output from the flash evaporation 106 that cryocondenses on the etched surface 102 and is then passed by a first curing station (not shown), for example electron beam or ultra-violet radiation, to initiate cross linking and curing. The plasma generator 100 has a housing 108 with a gas inlet 110. The gas may be oxygen, nitrogen, water or an inert gas, for example argon, or combinations thereof. Internally, an electrode 112 that is smooth or having one or more pointed projections 114 produces a glow discharge and makes a plasma with the gas which etches the surface 102. The flash evaporator 106 has a housing 116, with a monomer inlet 118 and an atomizing nozzle 120, for example an ultrasonic atomizer. Flow through the nozzle 120 is atomized into particles or droplets 122 which strike the heated surface 124 whereupon the particles or droplets 122 are flash evaporated into a gas that flows past a series of baffles 126 (optional) to an outlet 128 and cryocondenses on the surface 102. Although other gas flow distribution arrangements have been used, it has been found that the baffles 126 provide adequate gas flow distribution or uniformity while permitting ease of scaling up to

large surfaces **102**. In the method of radiation curing, a curing station (not shown) is located downstream of the flash evaporator **106**. The monomer may be an acrylate (**FIG. 1b**). This system was for planar layer coatings. With radiation curing, the time between deposition and curing permits flow of thicker coating layers leading to non-uniformity of coating on non-uniform surfaces or tilted planar surfaces.

Therefore, there is a need for an apparatus and method for coating fixtures with polymerized layers at a fast rate while avoiding flow of the coating.

10

SUMMARY OF THE INVENTION

The present invention is a method of making a plasma polymerized film on a fixture. More specifically, the method is for making a self-curing polymer layer, especially self-curing PML polymer layer on a fixture. The method relies upon a combination of flash evaporation with plasma enhanced chemical vapor deposition (PECVD) that provides the unexpected improvements of permitting use of low vapor pressure monomer materials in a PECVD process and provides a self curing from a flash evaporation process at a rate surprisingly faster (2 orders of magnitude or more) than standard PECVD deposition rates.

Another advantage of the present invention is the ability to make a conformal coating on a fixture. Because of rapid self curing, the monomer has less time to flow and is therefore more uniformly thick.

The method of the present invention has the steps of (a) flash evaporating a liquid monomer forming an evaporate; (b) passing the evaporate to a glow discharge electrode creating a glow discharge monomer plasma from the evaporate; and (c) cryocondensing the glow discharge monomer plasma on a substrate and crosslinking the glow discharge plasma thereon, wherein the crosslinking results from radicals created in the glow discharge plasma and achieves self curing.

It is an object of the present invention to provide a method combining flash evaporation with glow discharge plasma deposition for polymer coating a fixture.

An advantage of the present invention is that multiple layers of materials may be combined. For example, as recited in U.S. patents 5,547,508 and 5,395,644, 5,260,095, hereby incorporated by reference, multiple polymer layers, alternating layers of polymer and metal, and other layers may be made with the
5 present invention in the vacuum environment.

The subject matter of the present invention is particularly pointed out and distinctly claimed in the concluding portion of this specification. However, both the organization and method of operation, together with further advantages and objects thereof, may best be understood by reference to the following
10 detailed description in combination with the drawings wherein like reference characters refer to like elements.

BRIEF DESCRIPTION OF THE DRAWINGS

15 FIG. 1a is a cross section of a prior art combination of a glow discharge plasma generator with inorganic compounds with flash evaporation.

FIG. 1b is a chemical diagram of an acrylate.

FIG. 2a is an illustration of non-conformal coating.

FIG. 2b is an illustration of a conformal coating.

20 FIG. 3 is a cross section of the apparatus of the present invention of combined flash evaporation and glow discharge plasma deposition.

FIG. 3a is a cross section end view of the apparatus of the present invention.

FIG. 4 is a cross section of the present invention wherein the substrate
25 or fixture is the electrode.

FIG. 5 is a cross section of the present invention wherein a plurality of electrodes surrounds the substrate or fixture.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

30

The present invention is a method of conformally coating a fixture. Fixture is a discrete item including but not limited to plumbing fixtures for

example, faucets, spouts and/or valve handles or knobs, cabinetry fixtures, for example pulls or knobs, hinges, tools (especially hand tools), optical fixtures including reflectors, light covers, solar collectors and combinations thereof. A fixture is clearly distinct from and excludes a continuous item for example a
5 sheet, wire, or rope. A conformal coating on a portion of a fixture is illustrated in **FIG. 2b** wherein a coating surface **150** is geometrically similar to the fixture surface **160**.

The method of the present invention is done with the apparatus of **FIG. 3**, **FIG. 4** or **FIG. 5**, preferably within a low pressure (vacuum) environment or
10 chamber. Pressures preferably range from about 10^{-1} torr to 10^{-6} torr. The flash evaporator **106** has a housing **116**, with a monomer inlet **118** and an atomizing nozzle **120**. Flow through the nozzle **120** is atomized into particles or droplets **122** which strike the heated surface **124** whereupon the particles or droplets **122** are flash evaporated into a gas or evaporate that flows past a series of baffles
15 **126** to an evaporate outlet **128** and cryocondenses on the surface **102**. Cryocondensation on the baffles **126** and other internal surfaces is prevented by heating the baffles **126** and other surfaces to a temperature in excess of a cryocondensation temperature or dew point of the evaporate. Although other gas flow distribution arrangements have been used, it has been found that the
20 baffles **126** provide adequate gas flow distribution or uniformity while permitting ease of scaling up to large surfaces **102**. The evaporate outlet **128** directs gas toward a glow discharge electrode **204** creating a glow discharge plasma from the evaporate. In the embodiment shown in **FIG. 3**, the glow discharge electrode **204** is placed in a glow discharge housing **200** having an evaporate inlet **202**
25 proximate the evaporate outlet **128**. In this embodiment, the glow discharge housing **200** and the glow discharge electrode **204** are maintained at a temperature above a dew point of the evaporate. The glow discharge plasma exits the glow discharge housing **200** and cryocondenses on the surface **102** of the substrate (fixture) **104**. It is preferred that the substrate **104** is kept at a
30 temperature below a dew point of the evaporate, preferably ambient temperature or cooled below ambient temperature to enhance the cryocondensation rate. In this embodiment, the substrate **104** may be electrically grounded, electrically

floating, or electrically biased with an impressed voltage to draw charged species from the glow discharge plasma. If the substrate **104** is electrically biased, it may even replace the electrode **204** and be, itself, the electrode which creates the glow discharge plasma from the monomer gas. Substantially not electrically
5 biased means that there is no impressed voltage although a charge may build up due to static electricity or due to interaction with the plasma.

A preferred shape of the glow discharge electrode **204**, is shown in **FIG. 3a**. In this preferred embodiment, the glow discharge electrode **204** is separate from the substrate **104** and shaped so that evaporate flow from the evaporate
10 inlet **202** substantially flows through an electrode opening **206**. Any electrode shape can be used to create the glow discharge, however, the preferred shape of the electrode **204** does not shadow the plasma from the evaporate issuing from the outlet **202** and its symmetry, relative to the monomer exit slit **202** and substrate **104**, provides uniformity of the evaporate vapor flow to the plasma
15 across the width of the substrate while uniformity transverse to the width. The spacing of the electrode **204** from the substrate **104** is a gap or distance that permits the plasma to impinge upon the substrate. This distance that the plasma extends from the electrode will depend on the evaporate species, electrode **204**/substrate **104** geometry, electrical voltage and frequency, and pressure in
20 the standard way as described in detail in ELECTRICAL DISCHARGES IN GASES, F.M. Penning, Gordon and Breach Science Publishers, 1965, and summarized in THIN FILM PROCESSES, J.L. Vossen, W. Kern, editors, Academic Press, 1978, Part II, Chapter II-1, Glow Discharge Sputter Deposition, both hereby incorporated by reference. Alternatively, the electrode **204** may be
25 a plurality of electrodes distributed throughout the volume of the vacuum chamber defined by the housing **116**.

An alternative apparatus also suitable for batch operation is shown in **FIG. 4**. In this embodiment, the glow discharge electrode **204** is sufficiently proximate a part **300** (substrate) that the part **300** is an extension of or part of the
30 electrode **204**. Moreover, the part is below a dew point to allow cryocondensation of the glow discharge plasma on the part **300** and thereby coat the part **300** with the monomer condensate and self cure into a polymer layer.

Sufficiently proximate may be connected to, resting upon, in direct contact with, or separated by a gap or distance that permits the plasma to impinge upon the substrate. This distance that the plasma extends from the electrode will depend on the evaporate species, electrode **204**/substrate **104** geometry, electrical
5 voltage and frequency, and pressure in the standard way as described in **ELECTRICAL DISCHARGES IN GASSES**, F.M. Penning, Gordon and Breach Science Publishers, 1965, hereby incorporated by reference. The substrate **104**, **300** may be stationary or moving during cryocondensation. Moving includes rotation and translation and may be employed for controlling the thickness and
10 uniformity of the monomer layer cryocondensed thereon. Because the cryocondensation occurs rapidly, within milli-seconds to seconds, the part may be removed after coating and before it exceeds a coating temperature limit.

Another embodiment for non or marginally electrically conductive fixtures is shown in **FIG. 5** wherein electrode elements **204** surround the fixture **300**.

15 In operation, the method of the invention has the steps of (a) flash evaporating a liquid monomer forming an evaporate; (b) passing the evaporate to a glow discharge electrode creating a glow discharge monomer plasma from the evaporate; and (c) cryocondensing the glow discharge monomer plasma on a fixture **104**, **300** and crosslinking the glow discharge plasma thereon. The
20 crosslinking results from radicals created in the glow discharge plasma thereby permitting self curing.

The flash evaporating has the steps of flowing a monomer liquid to an inlet, atomizing the monomer liquid through a nozzle and creating a plurality of monomer particles of the monomer liquid as a spray. The spray is directed onto
25 a heated evaporation surface whereupon it is evaporated and discharged through an evaporate outlet. By using flash evaporation, the monomer is vaporized so quickly that reactions that generally occur from heating a liquid monomer to an evaporation temperature simply do not occur. Further, control of the rate of evaporate delivery is strictly controlled by the rate of liquid monomer
30 delivery to the inlet **118** of the flash evaporator **106**.

The liquid monomer may be any liquid monomer. However, it is preferred that the monomer material or liquid have a low vapor pressure at

ambient temperatures so that it will readily cryocondense. Preferably, the vapor pressure of the monomer material is less than about 10 torr at 83 °F (28.3 °C), more preferably less than about 1 torr at 83 °F (28.3 °C), and most preferably less than about 10 millitorr at 83 °F (28.3 °C). For monomers of the same
5 chemical family, monomers with low vapor pressures usually also have higher molecular weight and are more readily cryocondensable than higher vapor pressure, lower molecular weight monomers. Liquid monomer includes but is not limited to (meth)acrylate monomers, for example tripropyleneglycol diacrylate, tetraethylene glycol diacrylate, tripropylene glycol monoacrylate,
10 caprolactone acrylate, and combinations thereof.

In addition to the evaporate from the liquid monomer, additional gases may be added within the flash evaporator 106 through a gas inlet 130 upstream of the evaporate outlet 128, preferably between the heated surface 124 and the first baffle 126 nearest the heated surface 124. Additional gases may be organic
15 or inorganic for purposes included but not limited to ballast, reaction and combinations thereof. Ballast refers to providing sufficient molecules to keep the plasma lit in circumstances of low evaporate flow rate. Reaction refers to chemical reaction to form a compound different from the evaporate. Additional gases include but are not limited to group VIII of the periodic table, hydrogen,
20 oxygen, nitrogen, chlorine, bromine, polyatomic gases including for example carbon dioxide, carbon monoxide, water vapor, and combinations thereof. An exemplary reaction is by addition of oxygen gas to the monomer evaporate hexamethyldisiloxane to obtain silicon dioxide.

An advantage of the present invention is the ability to make conformal
25 coatings. Because of rapid plasma polymerization, the monomer has less time to flow and is therefore more uniformly thick even under conditions of substrate temperature and deposition rate that would produce non-conformal coatings using conventional deposition with significantly more time between condensation and polymerization.

30

CLOSURE

While a preferred embodiment of the present invention has been shown and described, it will be apparent to those skilled in the art that many changes
5 and modifications may be made without departing from the invention in its broader aspects. The appended claims are therefore intended to cover all such changes and modifications as fall within the true spirit and scope of the invention.

I claim:

1. A method for plasma enhanced chemical vapor deposition of low
5 vapor pressure monomeric materials onto a fixture in a vacuum environment,
comprising the steps of:
 - (a) making an evaporate by receiving a plurality of monomer
particles of the low vapor pressure monomeric materials as a spray into a flash
evaporation housing, evaporating said spray on an evaporation surface, and
10 discharging an evaporate through an evaporate outlet; and
 - (b) making a monomer plasma from said evaporate by passing
said evaporate proximate a glow discharge electrode and creating a glow
discharge for making said plasma from the evaporate; and
 - (c) condensing said monomer plasma onto said fixture.
- 15 2. The method as recited in claim 1, wherein the substrate is
proximate the glow discharge electrode and is electrically biased with an
impressed voltage, receiving the monomer plasma cryocondensing thereon.
- 20 3. The method as recited in claim 1, wherein said glow discharge
electrode is positioned within a glow discharge housing having an evaporate inlet
proximate the evaporate outlet, said glow discharge housing and said glow
discharge electrode maintained at a temperature above a dew point of said
evaporate and said substrate is downstream of said monomer plasma, and
25 electrically floating with an impressed voltage, receiving the monomer plasma
cryocondensing thereon.
- 30 4. The method as recited in claim 1, wherein the substrate is
proximate the glow discharge electrode and is electrically grounded, receiving
the monomer plasma cryocondensing thereon.

5. The method as recited in claim 1, wherein said monomer is selected from the group consisting of acrylate monomer, methacrylate monomer and combinations thereof.

5 6. The method as recited in claim 5, wherein said acrylate monomer is selected from the group consisting of tripropyleneglycol diacrylate, tetraethylene glycol diacrylate, tripropylene glycol monoacrylate, caprolactone acrylate, and combinations thereof;

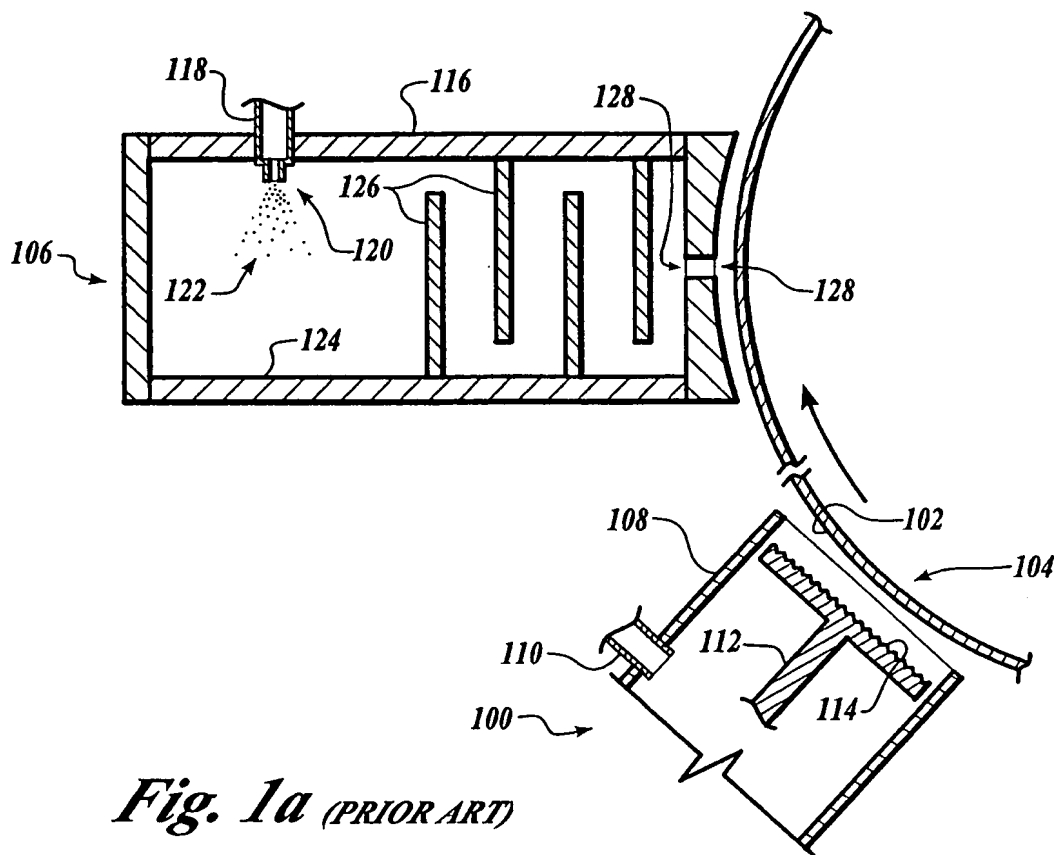
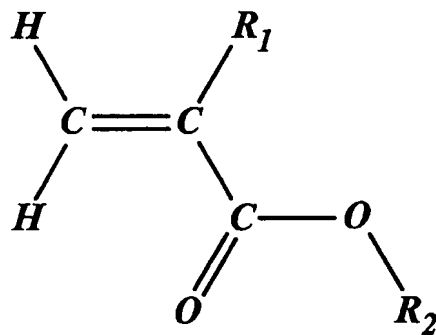
10 7. The method as recited in claim 1, wherein said substrate is cooled.

8. The method as recited in claim 1, further comprising adding an additional gas.

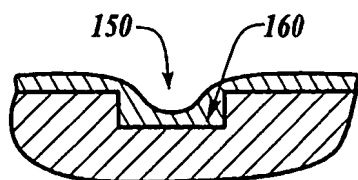
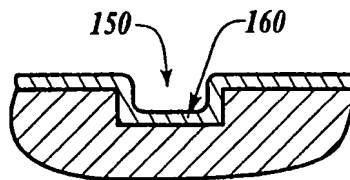
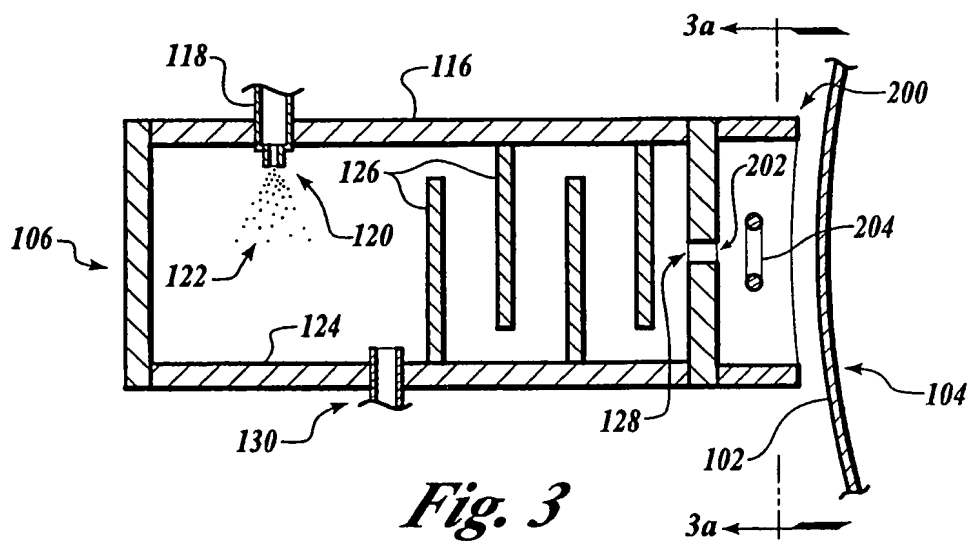
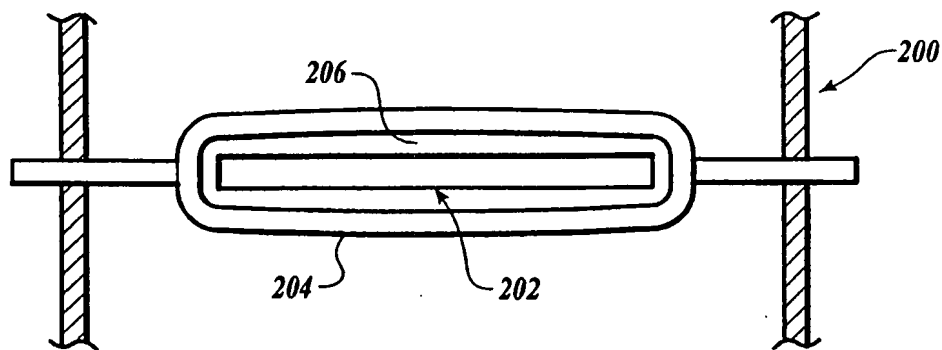
15 9. The method as recited in claim 8, wherein said additional gas is a ballast gas.

20 10. The method as recited in claim 8, wherein said gas is a reaction gas.

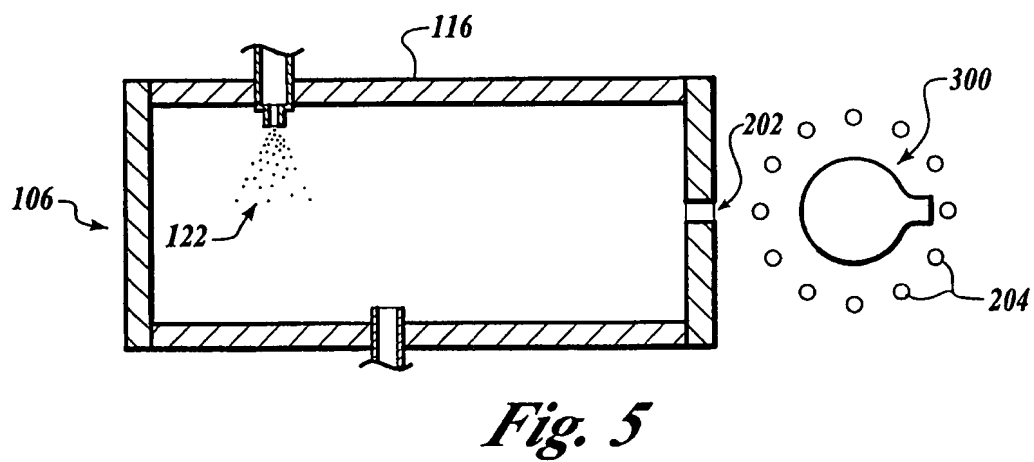
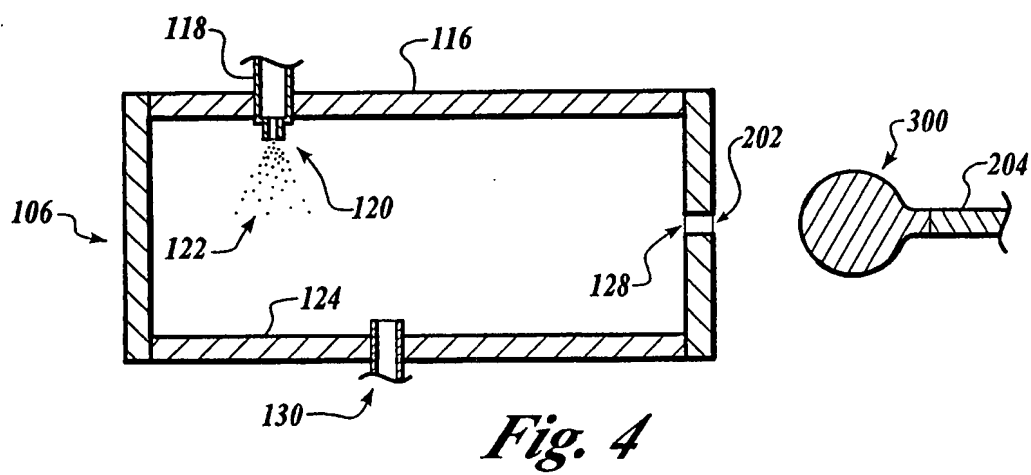
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*Fig. 1a (PRIOR ART)**Fig. 1b (PRIOR ART)*

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*Fig. 2a (PRIOR ART)**Fig. 2b**Fig. 3**Fig. 3a*

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INTERNATIONAL SEARCH REPORT

In International Application No
PCT/US 99/30071

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B05D7/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B05D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 99 16931 A (BATTELLE MEMORIAL INSTITUTE) 8 April 1999 (1999-04-08) the whole document	1-10
A	EP 0 340 935 A (SPECTRUM CONTROL INC) 8 November 1989 (1989-11-08) the whole document	1

☐ Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

28 April 2000

Date of mailing of the international search report

09/05/2000

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NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

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Brothier, J-A

INTERNATIONAL SEARCH REPORT

Information on patent family members

In International Application No
PCT/US 99/30071

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9916931 A	08-04-1999	NONE	
EP 0340935 A	08-11-1989	US 4842893 A JP 1316450 A US 5032461 A	27-06-1989 21-12-1989 16-07-1991